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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C08F 10/00, 4/651, 4/654</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 92/19658</b> <b>(43) International Publication Date:</b> 12 November 1992 (12.11.92)
<b>(21) International Application Number:</b> PCT/FI92/00082 <b>(22) International Filing Date:</b> 23 March 1992 (23.03.92) <b>(30) Priority data:</b> 912263 9 May 1991 (09.05.91) FI <b>(71) Applicant (for all designated States except US):</b> NESTE OY [FI/FI]; P.O. Box 310, SF-06101 Porvoo (FI). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> GAROFF, Thomas [FI/FI]; Borgströminkuja 4 K 104, SF-00840 Helsinki (FI). LEINONEN, Timo [FI/FI]; Hamarin koulu, SF-06650 Hamari (FI). IISKOLA, Eero [FI/FI]; Linnankoskenkatu 15 A 1, SF-06100 Porvoo (FI).		<b>(74) Agent:</b> BERGGREN OY AB; P.O. Box 16, SF-00101 Helsinki (FI). <b>(81) Designated States:</b> AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), NO, SE (European patent), US.  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i>
<b>(54) Title:</b> COARSE GRAINED POLYOLEFIN, PRODUCTION THEREOF AND A PROCATALYST CONTAINING A TRANSESTERIFICATION PRODUCT BETWEEN A LOWER ALCOHOL AND DIOCTYLPHTHALATE USED THEREFORE  <b>(57) Abstract</b>  The invention relates to a method for preparing polyolefins. In the polymerization, a procatalyst composition is being used, which has been prepared by contacting MgCl <sub>2</sub> , a lower alcohol, a titanium compound and a phthalic acid ester. The polyolefin is given the adequate coarseness by using a procatalyst of the said type, which has been prepared by carrying out a transesterification between the lower alcohol and the phthalic acid ester and by selecting dioctyl phthalate (DOP) as phthalic acid ester.		

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Coarse grained polyolefin, production thereof and a procatalyst containing a transesterification product between a lower alcohol and dioctylphthalate used therefore

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5       The invention relates to a method for preparing polyolefins by polymerizing an olefin with the aid of a procatalyst composition, which has been prepared by contacting  $\text{MgCl}_2$ , a lower alcohol, a titanium compound and a phthalic acid ester.

10       The invention also relates to a polyolefin which has been obtained by polymerizing an olefin in the presence of a procatalyst, which has been prepared by contacting  $\text{MgCl}_2$ , a lower alcohol, a titanium compound and a phthalic acid ester, as well as a procatalyst composition usable for the preparation of a coarse-grained and an even-grained polyolefin, which has been prepared by contacting  $\text{MgCl}_2$ , lower alcohol, a titanium compound and a phthalic acid ester.

20       Olefins, especially  $\alpha$  olefins, are often polymerized by means of a catalyst composition, in which the procatalyst consists of a compound of a transition metal of groups IV-VI of the periodic system, and the cocatalyst is a compound of a metal of groups I-III of the periodic system, which activates the procatalyst by reduction. The so-called Ziegler-Natta procatalyst has been further developed by using an inert carrier as a support of the transition metal compound, the transition metal compound being superposed on the inert carrier in order to improve the activity of the procatalyst as it catalyzes the polymerization reaction.

30       However, under the effect of this procatalyst composition, the asymmetrical olefin monomers are often polymerized into different stereoisomeric polymers,

yielding for instance mixtures of isotactic, atactic and syndiotactic polymers, from which the desired stereoisomer has to be separated by means of washing and similar steps, which are often complicated. In order to prepare a polymer having a basically specific stereo-specific form, for instance an isotactic polyolefin, out of an asymmetrical olefin monomer, the effect of the catalyst on the stereospecificity of the yielded product has been enhanced by adding a donor compound to the catalyst.

Owing to its specific steric structure, the donor compound promotes the settling of the monomer molecule into a given position in the catalyst particle at the end of the growing polymer molecule, and thus the molecule chain of the polymer gets a given stereoisomeric structure and the polymer product obtained corresponds more or less to the desired product as a function of the selected donor compound.

There are two ways of adding the donor to the catalyst: a so-called internal donor is added already to the procatalyst mixture of the transition metal compound and the carrier, or then the donor is added to the mixture of the monomer and the catalyst component only in the polymerization reactor together with the cocatalyst, and in this case a so-called external donor is concerned. A donor compound may of course be used in both the steps, and then the donor may be the same or a different compound in the various steps.

All monomers are asymmetrical, i.e. stereospecifically polymerizable monomers, except ethene, the unsaturated carbons of which have hydrogen substituents, and also in the rare case in which all the secondary groups are identical, tetramethyl-ethylene for instance. A certain

stereospecific form is desirable because the properties of the yielded polymer for a given purpose are enhanced, for example isotactic polyolefins are better crystallized, their bulk density is higher, their mechanical properties are better, being for instance more resistant, etc. The adhesion characteristics of the atactic form are usually better than with other tactic forms and thus they are suitable for glue implementations among others.

When polymerizing assymmetrical olefin monomers, i.e. when at least one of the groups connected to the carbon atoms bound by an unsaturated bond is different, the catalyst may comprise a compound enhancing the stereospecificity of the catalyst, i.e. an electron donor, which, due to its electron donor character, may be connected to some other catalyst structure, and due to its steric action, may guide the monomer molecule of the polymer chain into such a position, that the yielded polymer molecule has a stereospecific structure in some respect. Such donors are a great number of various organic compounds, such as esters, carboxylic acids, alcohols, ketones, aldehydes, nitriles, amides, amines, organic phosphor and silicon compounds, etc. These compounds also have other effects on the characteristics of the catalyst, one such being that the activity of the catalyst varies according to the donor used in each case. If the donor is a carboxylic acid ester, it is usually an aromatic carboxylic acid ester, e.g. benzoates, phthalates, toluates, anisates, etc. The optimal donors among these are dialkyl phthalates.

Thanks to the so-called replica process, the physical structure of the procatalyst carrier is reproduced throughout the procatalyst composition and eventually also in the polymer product, and this means that the

morphology of the procatalyst composition is very important in view of the polymerization.

Combinations of various donors are also known in the field. Thus, the JP patent specifications 59172507, 59206409, 59206415, 59206416, 59206424, 60262804, 61103910 and 61108614 disclose a procatalyst composition, which has been prepared from  $MgCl_2$ , 2-ethyl hexylalcohol, titanium tetrachloride, di-isobutyl phthalate and in some cases from phthalic acid anhydride.

The patent family including the patent specifications DE 3 540 699, EP 226 003 and US 4 761 461, discloses a method for preparing propene polymers by means of a procatalyst composition, which has been obtained by contacting  $MgCl_2$ , alkanol, such as ethanol, phthalic acid ester, such as di-isobutyl phthalate, and titanium tetrachloride under given conditions. The phthalic acid may be added either at the stage when  $MgCl_2$  and ROH react with each other, or at the stage when the reaction product of  $MgCl_2$  and alkanol is reacted with titanium tetrachloride.

The procatalysts and methods described above have affected the particle size and shape of the polymer product and the particle size distribution to a very small extent. Thus, a great amount of fine fraction has been produced, which is detrimental for the treatment of polyolefins.

The object of the invention is to provide an active and stereospecific procatalyst composition. Another object is to reduce the titanium and donor contents of the catalyst and thus of the polymer, since these bring about colour problems and aromaticity in the polymers. The purpose is

in particular a catalyst and a method which allow to increase the particle size of the polymer and to reduce the share of its fine fraction.

5 The purposes of the invention have now been achieved with a new method for preparing polyolefins, which is mainly characterized by the features presented in the characterizing part of claim 1. The invention also relates to a new polyolefin, which is mainly  
10 characterized by the features presented in the characterizing part of claim 7, and a new procatalyst composition suitable for the preparation of coarse-grained and even-grained polyolefins, which is mainly characterized by the features presented in the  
15 characterizing part of claim 9.

Hence, it has been discovered, that when using a procatalyst composition prepared by contacting  $MgCl_2$ , lower alcohol, a titanium compound and phtalic acid  
20 ester, the particle size of the polyolefin product can be increased and the share of the fine fraction decreased by carrying out a transesterification between the lower alcohol and the phtalic acid ester during the preparation of the procatalyst, and by selecting dioctyl  
25 phthalate DOP as phtalic acid ester.

In the polymerization method according to the invention, the  $MgCl_2$  carrier of the used procatalyst composition may be used as such or combined with silica, e.g. by  
30 absorbing a solution or slurry containing  $MgCl_2$  into the silica. It is also important that the  $MgCl_2$  used is clean and anhydrous.

The lower alcohol used in the method may be any  $C_1$ - $C_4$   
35 alcohol. Advantageous alcohols are methanol and ethanol,



especially ethanol.

Since, under the effect of the so-called replica process, the physical structure of the catalyst carrier is reproduced throughout the catalyst composition, and this is again reproduced in the yielded polymer product, it is crucial to make the physical structure of the carrier, i.e. the morphology, advantageous, in other words, similar to the desired product. This can be achieved by using two different procedures, which may of course be combined: chemically, i.e. by treating the carrier with a specific or a number of specific chemicals, or physically, i.e. by grinding the carrier in a ball mill or a jet blowing mill.

One may also proceed by first making an adduct between the carrier, in this case expressly  $\text{MgCl}_2$ , and a lower alcohol, advantageously ethanol, and melting the adduct, injecting the melt by gas into a cooled solvent or a cooled gas, whereby the adduct is crystallized into a morphologically advantageous form, and this crystallized adduct is used as a catalyst carrier (cf. FI 862459).

The titanium compound used for the preparation of the procatalyst composition of the method according to the invention is advantageously an organic or inorganic titanium compound with the oxidation degree 3 or 4. When needed, the titanium compound can be admixed with other transition metal compounds, such as vanadium, zirkonium, chromium, molybdene, wolfram compounds. The titanium compound is usually halogenide or oxyhalogenide, an organic metal halogenide or a purely metalorganic compound, in which only organic ligands have been bound to the transition metal. Titanium halogenides, in particular  $\text{TiCl}_4$ , are especially advantageous.

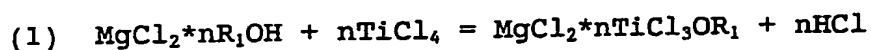
The phthalic acid ester used in the method is dioctyl phthalate, since only this substance yields the desired coarseness and low fine fraction content of the polymer product. The advantages are unexpected and differ from the results yielded by other phthalic acid esters. It is also advantageous that the dioctyl phthalate acts as a so-called electron donor of the catalyst composition with the purpose to improve the activity and/or stereospecificity of the obtained polymer. In the synthesis, the molar ratio of the dioethyl phthalate to the magnesium halogenide is advantageously of the order of c. 0.2.

The transesterification can be accomplished e.g. by choosing a pair of phthalic acid ester - lower alcohol which is transesterified under normal preparation conditions, either spontaneously or by means of a catalyst that does not damage the procatalyst composition. However, it is often necessary to apply a raised temperature in order to bring about the transesterification. In this case, the transesterification is advantageously carried out at a temperature in the range of 110-150°C and preferably in the range of 130-140°C.

Since the boiling point of liquid  $\text{TiCl}_4$  under normal pressure is about 136°C, the treatment by means of this, i.e. the so-called titanization, can normally be performed only at a temperature lower than this. Given that hydrocarbon solvents such as heptane, hexane or pentane are usually used as a titanization medium, and these have a markedly lower boiling point, the titanization temperature is below 100°C in practice, a temperature at which no transesterification takes place. Thus, in order to produce a transesterification, solvents boiling at a higher temperature should advantageously be

applied, for instance nonane (boiling point 151°C) and decane (boiling point 174°C) are recommended. Thus the boiling point of  $\text{TiCl}_4$  is approached and even exceeded in terms of the titanization temperature, allowing a simultaneous transesterification reaction.

According to one embodiment, the transesterification takes place so that the adduct of magnesium chloride and lower alcohol  $\text{MgCl}_2 \cdot n\text{R}_1\text{OH}$ , in which  $n$  is 1-6, is treated with a titanium compound, e.g. is titanized with  $\text{TiCl}_4$ , apparently generating the following reaction:



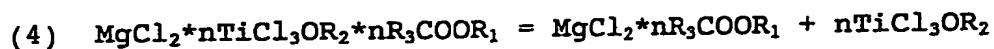
As the donor, i.e. phthalic acid ester, is added to this titanized carrier, an adduct formed by all the components is probably produced:



As this adduct can be transesterified at a temperature above 100°C and advantageously above c. 130°C, the ester groups  $\text{R}_1$  and  $\text{R}_2$  change places:



As the catalyst residue is removed by extracting, an adduct of the carrier and the ester donor is obtained, in which the group deriving from the ester alcohol has changed:



In case sufficient titanium remains on the carrier, it will act as an active element of the procatalyst.

Otherwise the titanization is renewed after the above treatment in order to ensure a sufficient titanium concentration and thus an activity. The titanium separation of formula (4) relates to the inactive part of the titanium.

Consequently, a procatalyst composition for the polymerization of olefins has been provided in the present invention, the composition having a low titanium and donor content with regard to the activity of the catalyst. According to one embodiment, the procatalyst composition contains 2.0% by weight of Ti at the most. Its molar ratio donor/mg is advantageously in the range of 0.03-0.06 and/or its donor concentration in the range of 4-6% by weight. The phthalic acid ester alkoxy group has 8 carbon atoms, whereby the activity of the procatalyst composition is advantageously c. 800 kg PP/g Ti when using triethyl aluminium as a catalyst and cyclohexylmethyl dimethoxysilane as an external donor.

The procatalyst composition for the polymerization of olefins according to the invention is advantageously prepared

- a) by reacting the adduct of  $MgCl$  and lower alcohol with the titanium compound,
- b) by reacting the product of step a) with dioctyl phthalate under conditions in which the transesterification of dioctyl phthalate and lower alcohol takes place,
- c) by washing the product,
- d) by optionally reacting the end product of step c) with the titanium compound (i.e. a second treatment).

In the polymerization method according to the invention, the polymerization is advantageously carried out in the

presence of an organometallic cocatalyst, such as trialkyl aluminium (e.g. triethyl aluminium), and advantageously of an external donor similar to cyclohexylmethyl dimethoxysilane. The polymer produced according to the invention contains a small amount of titanium and donor, among others, and resembles morphologically a relatively coarse catalyst composition. Propene is an advantageous olefin monomer.

According to a preferred embodiment of the invention, the catalyst and/or polymer particles are formed by agglomerating a more finely divided material. The catalyst particles produced advantageously have a size distribution such that 90% by weight has an average diameter above 200  $\mu\text{m}$ . The average diameter of the corresponding polymer particles is advantageously of the order of c. 1-2 mm, particles having a diameter under c. 1 mm being preferably absent.

An olefin polymerization method is described as an exemplified case below, in which propene is polymerized with a catalyst composition, in which a spray crystallized  $\text{MgCl}_2 \cdot 3 \text{ EtOH}$  adduct is used as a carrier, which has subsequently been titanized with  $\text{TiCl}_4$  in a hydrocarbon solvent in the presence of di-alkyl phthalates of various lengths. By means of the procatalyst composition and the trialkyl aluminium cocatalyst (triethyl aluminium TEA) thus obtained as well as of an external donor (cyclohexyl methoxy dimethylsilane CMMS) the propene was polymerized in a hydrocarbon solvent. If a sufficiently high titanizing temperature is applied, a transesterification will take place between the ethoxy groups deriving from the carrier-adduct and the long alkyl groups of the donor, yielding diethyl phthalate (DEP) as a donor compound. The following examples are merely intended to illustrate the invention.

ExamplesExamined donors

5 donors were examined in the test series. The donors are given in table 1. The donors examined were propylhexyl phthalate (PrHP), dioctyl phthalate (DOP), di-isodecyl phthalate (DIDP) and ditridecyl phthalate (DTDP). Di-isobutyl phthalate (DIBP) was also included in the test series.

Table 1

Examined internal donors

Test Length of the alkyl Donor group	Molar mass g/mol	Density g/ml
1 4 DIBP	278	1,00
2 6 PrHP	292	0,95
3 8 DOP	390	0,96
4 10 DIDP	446	0,96
5 13 DTDP	530	0,91

Catalyst synthesis

0.1 moles of  $\text{MgCl}_2 \cdot x \text{ EtOH}$  was suspended under inert circumstances in 250 ml of decane in a reactor. The solution was cooled to a temperature of  $-15^\circ\text{C}$  and 300 ml of cold  $\text{TiCl}_4$  was added. This was followed by a controlled heating to a temperature of  $+20^\circ\text{C}$ . At this temperature, 0.02 moles of internal donor was added. In all the catalyst syntheses, the molar ratio between the donor and  $\text{MgCl}_2$  was 0.2. When all the synthesis reagents were present, the temperature was raised to  $135^\circ\text{C}$ . Both the first and the second titanization were carried out at this temperature. The catalyst synthesis was ended by performing a normal washing of the reaction mixture.

In order to investigate the particle size of the produced

procatalyst, the particle size distribution of the product was measured and each sample was microscopically photographed. In addition, the chemical composition of the procatalyst was measured by analyzing their T, Mg and donor contents. In order to examine the changes in the crystal structure, X-ray diffraction spectrums were also taken.

#### Test polymerization

All the catalysts were submitted to a test polymerization under the following polymerizing conditions. A 2 l. bench reactor was used as a reaction vessel. 20-30 mg of procatalyst was used in the test polymerization. This amount was mixed with 620 ul of triethyl aluminium and 200 ul of a 25% solution of CMMS in 30 ml of heptane. The polymerizations were carried out at a temperature of +70°C and under a propene monomer pressure of 10 bar. The partial pressure of hydrogen was 0.2 bar during the polymerization. The polymerization lasted 3 hours. At the beginning of the test, the prepolymerization took place during the 10 minutes in the course of which the temperature and the pressure reached the desired polymerization conditions. The activity was measured on the basis of the polymerization yield. The soluble portion of the polymer was measured by evaporating a measured portion from the polymerization solution. Under these standard polymerization conditions, a polymer material was prepared, the MFR (...) of which was approx. 8.

#### Characterization of the polymerization batches

The bulk density and particle size distribution (PSD) of all the polymerization drives were measured. The isotacticity index was measured with the help of heptaneluation and the isotacticity was determined on the basis of the results obtained from the evaporation

residue measurements. The melt viscosity was measured at a temperature of 230°C by using a weight of 2.16 kg. All the polymerization batches were microscopically photographed in view of further documentation and comparisons. In order to characterize the melt behavior of the material, differential scanning calorimetric curves (DCS curves) were carried out. The specific area and the pore volume distribution were measured with the aid of an Hg porosimetric equipment.

### Results

Table 2 presents the symbols of all the catalysts and the corresponding polymers.

Table 2

Symbols of the catalysts and polymers used in the study

Alkyl group length	Catalyst symbol	Polymer symbol
4	C-C-4	1 PP-C-4
6	C-C-6	2 PP-C-6
8	C-C-8	3 PP-C-8
10	C-C-10	4 PP-C-10
13	C-C-13	5 PP-C-13

### Titanium content of the catalyst

Table 3 indicates the magnesium and titanium contents of the catalysts. The titanium content is also presented in figure 1. The results showed that, with a substantially constant Mg content, a systematic decrease of the Ti content was observed in the catalyst series. The longer the alkyl chain of the alkoxy group of the electron donor, the smaller the Ti content of the final procatalyst. The Ti content of the last catalyst in the range was 1.6% by weight. This is a 60% lower value than the 4% obtained in the standard synthesis and up to 30% lower than the titanium content found in commercial high



yield catalysts. These results showed that the combination of transesterification and the washing effect of  $\text{TiCl}_3 \cdot x \text{OEt}$  is enhanced by using higher phthalic acid esters.

### Table 3

Mg and Ti contents of the catalysts

Alkyl chain length	Mg (%)	Ti (%)
4	18.1	2.4
6	20.8	2.2
8	22.0	1.9
10	20.0	1.9
13	17.3	1.6

### Catalyst yield of the catalyst synthesis

Table 4 indicates the respective catalyst yields of each catalyst synthesis, and the results are graphically presented in figure 2. The same trend can be observed as in the first measurement, i.e. as the phthalic alkyl chain increases and the titanium content decreases, the catalyst yield also decreases. The yield is very slightly reduced, only 25%, which is explained by the decreased  $\text{TiCl}_4$  content of the catalyst and the weight reduction produced by the replacement of an electron donor with a high molar mass by one with a lower molar mass. The reduced catalyst yield is also explained by the reduction of the total donor content.

### Table 4

Catalyst yield of the catalyst synthesis

Alkyl group length	Yield (g)
4	13.3
6	10.0
8	12.4
10	9.1

15

13

9.2

Donor content of the catalysts

The donor composition of the catalysts was measured by liquid chromatography by using the HPLC method. The results are listed in table 5 and are graphically presented in figure 3. In all the catalysts, a small fraction of mixed esters and a small fraction of phthalic acid anhydride were observed. As seen in figure 3, the transesterification was not complete for the first catalyst of the test series. The transesterification degree of DIBP was only 70%. This implies that DIBP is not completely transesterified at a temperature of 135°C. In all the other syntheses, the transesterification was complete. Only traces of the original ester were found in their products. The amount of transesterified DEP diethyl phthalate found in the catalysts was essentially constant and near 5%. This equals a D/Mg ratio of 0.03-0.04 (D = donor), which is even a lower value than the one obtained as DIBP was transesterified at a temperature of 143°C.

These results show that the transesterification is improved if longer alkyl chains are used in the phthalic acid esters. They also show that a low molar ratio electron donor/MgCl<sub>2</sub> is obtained.

Table 5

Donor composition of the catalysts. PA = acid anhydride and IE = mixed esters produced during the transesterification

Alkyl group length	Original (%)	DEP (%)	PA (%)	IE (%)
4	3.6	4.0	1.3	1.0
6	0.2	5.3	0.3	0.9
8	0.3	4.8	0.7	0.4
10	0.4	5.3	1.1	0.5

13                                      0.2                      5.9    0.7    0.4

#### Particle size distribution of the catalysts (PSD)

The PSD of the catalysts was also measured and the results are given in table 6. Figure 4 shows the share in which more than 90% of the particles had an average particle diameter as a function of the alkyl chain length. The results show that a change of the donor compositions entails a marked change of the PSD. At the same time it was noted that the catalyst particles agglomerate as higher phthalic acid esters are being used. The effect was most drastic when dioctyl phthalate was used, appearing as a noticeable agglomeration. This agglomeration appears in the PSD curves of figures 5, 6 and 7, as well as the microscopic pictures in figures 8, 9 and 10. The results also showed that the agglomeration decreased again when higher phthalic acid esters were used. By using DIDP (C = 10), very beautifully shaped catalyst particles were obtained, having a diameter of about 140  $\mu\text{m}$ . This appears from figure 10.

Table 6

Particle size distribution of the catalysts

Alkyl group length	D (0.9) $\mu\text{m}$	D (0.5) $\mu\text{m}$	D (0.1) $\mu\text{m}$
4	117	62	34
6	127	68	36
8	218	76	17
10	138	56	18
13	140	69	36

#### X-ray diffraction spectrums of the catalysts

The tranesterification yielded a new procatalyst structure, which appears in the double peak at 13-15°. In order to observe the effect of higher phthalic esters X-ray diagrams were taken of all the catalysts in the t st series. Table 7 lists the crystal dimensions deduced from

the diagrams and the results are also shown in figure 11. According to the results, the crystal was systematically broadened as the alkyl chain of the ester was lengthened. DTDP yielded 25% broader crystals than DIBP.

Figure 12 shows the X-ray diffraction spectrum of the catalyst C-C-6. According to the diagram, recrystallization appeared in the  $\text{MgCl}_2$  crystal grating, showing as a sharpening of the crystal peak at  $30^\circ$  and  $35^\circ$ . The forming of the double peak at  $13-15^\circ$  can also be seen.

Table 7

Crystal dimensions of the  $\text{MgCl}_2$  materials of the catalysts

Section levels			
Alkyl group length	Height(nm)	Width(nm)	Growth (%)
4	1.8	7.9	0
6	2.1	7.9	0
8	1.9	8.4	6
10	2.3	9.3	18
13	2.2	9.8	24

Area and pore volume of the catalysts

The area and the pore volume of the catalysts were measured. The results are listed in table 8. According to these, the area of the catalysts remained almost constant regardless of the donor used in the synthesis. The specific area obtained was of the order of about  $300 \text{ m}^2/\text{g}$ . Conversely, the pore volume increased as donors with longer chains were used. In the last catalyst of the series an increase of up to 60% was observed. The increase of the pore volume can partly be explained by the agglomerizing of the catalyst particles.

Table 8

## Specific area and pore volumes of the catalysts

Alkyl group length	Area (m <sup>2</sup> /g)	Pore volume (ml/g)
4	348	0.524
6	316	0.738
8	311	0.581
10	339	0.776
13	292	0.814

Activity of the catalysts

All the catalysts were test polymerized in the conditions described above. The results are given in table 9 and figure 13. The activity based on the weight of the catalyst and the polymer remained constant for the entire catalyst range and was about 16 kg/g of cat. Expressed as the unit kg PP/g of Ti, the activity increased systematically. This was due to the fact that the Ti content decreased accordingly as higher phtalic acid esters were used. Thus, an activity value of 1019 kg PP/g of Ti was obtained for the last catalyst in the range. When decane was used as an activating medium, the activity of the catalyst decreased slightly.

Table 9

## Activity of the catalysts

Alkyl group length	Activity (kg PP/g of cat.)	Activity (kg PP/g of Ti)
4	16.6	692
6	15.6	709
8	16.2	853
10	16.6	874
13	16.3	1019

Particle size distribution (PSD) of the polymers

Table 10 shows the PSD of the polymers together with a fine fraction, i.e. the total amount of particles under 1 mm. The amount of the fine fraction is also graphically

presented in figure 17.

The PSFD results of the polymers follow the same pattern as the PSD results of the catalysts, i.e. a marked agglomerating effect was observed especially with DOP esters. When still greater chain lengths were used, the agglomerating trend decreased. This appears in the PSD diagrams of figures 14, 15 and 16. The share of the fine fraction ( $D < 1 \text{ mm}$ ) was generally high ( $> 15\%$ ), however for DOP is was practically non-existent. The absence of the fine fraction can be explained by the agglomeration in this case.

Table 10

Particle size distribution of the polymers

Alkyl content/ number of C atoms	Share (% by weight) of the material having a diameter d (mm) within the following range						
	d>2.0	2.0>d	1.0>d	0.5>d	0.18>d	0.1>d	d<0.056
		>1.0	>0.5	>0.18	>0.1	>0.056	

4	12.0	67.4	18.5	1.8	0.2	0.1	20.6
6	10.7	71.3	17.7	0.2	0.1	0.0	18.0
8	95.0	3.1	1.1	0.5	0.2	0.1	1.9
10	14.6	69.4	15.5	0.5	0.2	0.0	16.0
13	52.1	30.4	17.1	0.2	0.1	0.1	17.5

Bulk density of the polymers

The bulk density decreased as higher phthalic acid esters were used in the transesterification synthesis. The results are listed in table 11 and presented in figure 18. According to the figure, the bulk density is actually a function of the agglomerating tendency. The more the polymer is agglomerated, the lower the bulk density. When

DIBP esters are used, there is practically no agglomeration, whereby the bulk density will be 0.46 g/ml. If again DOP esters are used, a marked agglomeration will take place and the bulk density drops to 0.33 g/ml.

#### Table 11

Bulk density of the polymers

Alkyl group length	Bulk density (g/ml)
4	0.46
6	0.44
8	0.33
10	0.37
13	0.39

#### Melt viscosity of the polymers

The chain length of the ester did not have a great impact on the melt viscosity. The results are shown in table 12.

#### Table 12

Melt viscosity of the polymers

Alkyl group length	Melt viscosity (2.16 kg)
4	10.5
6	9.3
8	10.0
10	7.3

#### Molecular weight of the polymers

No systematic changes in the molecular weight distribution were observed as the esters changed. All the results are listed in table 13. The results correspond to the ones normally obtained in standard polymerization.

#### Table 13

Molecular weight distribution of the polymers

	Alkyl group length	Mn	Mw	Mv	D
	4	58 100	273 000	223 000	4.7
	4	58 800	274 000	222 000	4.7
5	6	56 000	281 000	225 000	5.2
	6	55 200	289 000	233 000	5.2
	8	60 100	273 000	221 000	4.6
	8	60 700	279 000	228 000	4.6
10	10	73 800	331 000	269 000	4.5
	10	74 600	334 000	270 000	4.5

#### DSC measuring results of the polymers

Table 14 presents a list of fusion points, crystallization points and crystallization percentages of the polymers. These measurements did not either reveal any systematic dependency of the esters used. The point of fusion is about 161°C and the crystallization temperature about 114°C. The crystallization was about 51-52%. A number of fusion curves are presented in figures 19, 20 and 21.

It can be generally noted that there is a correlation between the titanization temperature and the crystallization temperature of the catalyst. A higher titanization temperature yields a purer catalyst and a more homogenous polypropene. This again increases the crystallization of the polymer and reduces its crystallization temperature. Figure 22 presents a schematic view of the correlation between the titanization temperature of the catalyst and the crystallization temperature of the polymer.

#### Table 14

Fusion temperature, crystallization temperature and



crystallization percentage of the polymers

Alkyl group length	Fusion point (°C)	Cryst.point (°C)	Crystall. (%)
4	161.6	114.1	51.4
6	161.0	113.5	50.7
8	161.6	113.4	51.8
10	161.6	114.7	52.7
13	158.3	114.8	51.9
	164.3		

#### Specific area and pore volume distribution of the polymers

Table 15 gives the results of the area and pore volume measurements. The measurements were carried out by means of an Hg porosimeter. The results corresponded to the ones obtained with the corresponding catalysts. As shown in figure 23, the specific area of the pores decreases only slightly when higher phthalic acid esters are used in the transesterification synthesis. The pore volume, again, increased linearly according to the alkyl chain length of the phthalic acid ester, as in figure 24. The increase was about 100% for the last polymer of the range, compared to the first polymer of the range. According to figure 25, DIDP greatly increased the share of the macroporous fraction (10-100  $\mu\text{m}$ ), whereas DTDP increased the share of the micropores (1-10  $\mu\text{m}$ ).

Table 15

Specific area and pore volume of the polymers, median diameter of the pores

Alkyl group length	Area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{ml/g}$ )	Pore diameter ( $\mu\text{m}$ )
4	53.5	0.22	1.2
6	52.4	0.25	4.9
8	58.5	0.24	1.5
10	46.0	0.35	26.3
13	41.2	0.41	18.8

Claims

1. A method for producing polyolefins by polymerizing olefins by means of a procatalyst composition, which has been prepared by contacting  $\text{MgCl}_2$ , a lower alcohol, a titanium compound and a phthalic acid ester, characterized in that a coarser polyolefin is produced by using a procatalyst of the said type, which has been prepared by carrying out a transesterification between the lower alcohol and the phthalic acid ester, and by selecting dioctyl phthalate (DOP) as the said phthalic acid ester.

2. A method according to claim 1, characterized in that the olefin used in the method is propene.

3. A method according to claim 1 or 2, characterized in that the lower alcohol is ethanol.

4. A method according to claim 1, 2 or 3, characterized in that the titanium compound is  $\text{TiCl}_4$ .

5. A method according to any of the preceding claims, characterized in that the olefin is polymerized by means of an organometallic cocatalyst such as trialkyl aluminium and preferably by means of an external donor such as cyclohexylmethyl dimethoxysilane.

6. A method according to any of the preceding claims, characterized in that the coarse-grained polyolefin is prepared by agglomeration of the polyolefin material produced in the polymerization.

7. A polyolefin produced by the polymerization of olefin in the presence of a procatalyst, which has been prepared by contacting  $\text{MgCl}_2$ , a lower alcohol, a titanium compound and phthalic acid ester, characterized in that it has a

coarseness obtained by using a procatalyst of the above type, which has been produced by a trans-esterification of the lower alcohol and the phtalic acid ester and by selecting dioctyl phthalate as a phtalic acid ester.

5 8. A polyolefin according to claim 7, characterized in that the average diameter of its particles is of the order of about 1-2 mm, particles having a diameter under about 1 mm being essentially absent.

.0 9. A procatalyst composition usable for preparing polyolefins with a coarse and regular grain structure, the procatalyst composition having been produced by contacting  $MgCl_2$ , a lower alcohol, a titanium compound and  
.5 a phtalic acid ester, characterized in that a trans-esterification has been carried out between the lower alcohol and the phtalic acid ester and in that dioctyl phthalate (DOP) is used as the said phtalic acid ester.

!0 10. A procatalyst composition according to claim 9, characterized in that the transesterification has been carried out at a temperature in the range of 110°C to 150°C, preferably in the range of 130°C to 140°C.

!5 11. A procatalyst composition according to claim 9 or 10, characterized in that the transesterification has been carried out in a solvent having a boiling point above the transesterification temperature, preferably in nonane or decane.

!0 12. A procatalyst composition according to claim 9, 10 or 11, characterized in that the lower alcohol is ethanol.

!5 13. A procatalyst composition according to any of claims 9 to 12, charact rized in that th titanium compound is

TiCl<sub>4</sub>.

14. A procatalyst composition according to any of claims 9-13, characterized in that it has been produced by

5 a) reacting an adduct of MgCl<sub>2</sub> and a lower alcohol with the titanium compound,

b) by reacting the product of step a) with dioctyl phthalate (DOP) under conditions in which a transesterification takes place between the dioctyl  
10 phthalate and the lower alcohol,

c) by washing the product or

d) by optionally reacting the product of step c) with a titanium compound.

15 15. A procatalyst composition according to any of claims 9-14, characterized in that 90% by weight of its particles have an average diameter with a length above 200 μm.

20 16. A procatalyst composition according to any of claims 9-14, characterized in that its particles are agglomerates.

## AMENDED CLAIMS

[received by the International Bureau on 9 October 1992 (09.10.92) ;  
original claims 1 and 10 amended ; remaining claims unchanged (3 pages)]

1. A method for producing polyolefins by polymerizing  
olefins by means of a procatalyst composition, which has  
been prepared by contacting  $\text{MgCl}_2$ , a lower alcohol, a  
5 titanium compound and a phthalic acid ester, characterized  
in that a coarser polyolefin is produced by using a  
procatalyst of the said type, which has been prepared by  
carrying out a transesterification between the lower  
alcohol and the phthalic acid ester at a temperature in  
10 the range of 110 to 150°C, and by selecting dioctyl  
phthalate (DOP) as the said phthalic acid ester.
2. A method according to claim 1, characterized in that  
the olefin used in the method is propene.
- 15 3. A method according to claim 1 or 2, characterized in  
that the lower alcohol is ethanol.
4. A method according to claim 1, 2 or 3, characterized  
20 in that the titanium compound is  $\text{TiCl}_4$ .
5. A method according to any of the preceding claims,  
characterized in that the olefin is polymerized by means  
of an organometallic cocatalyst such as trialkyl  
25 aluminium and preferably by means of an external donor  
such as cyclohexylmethyl dimethoxysilane.
6. A method according to any of the preceding claims,  
characterized in that the coarse-grained polyolefin is  
30 prepared by agglomeration of the polyolefin material  
produced in the polymerization.
7. A polyolefin produced by the polymerization of olefin  
in the presence of a procatalyst, which has been prepared  
35 by contacting  $\text{MgCl}_2$ , a lower alcohol, a titanium compound  
and phthalic acid ester, characterized in that it has a

coarseness obtained by using a procatalyst of the above type, which has been produced by a trans-esterification of the lower alcohol and the phtalic acid ester and by selecting dioctyl phthalate as a phtalic acid ester.

5

8. A polyolefin according to claim 7, characterized in that the average diameter of its particles is of the order of about 1-2 mm, particles having a diameter under about 1 mm being essentially absent.

10

9. A procatalyst composition usable for preparing polyolefins with a coarse and regular grain structure, the procatalyst composition having been produced by contacting  $MgCl_2$ , a lower alcohol, a titanium compound and a phtalic acid ester, characterized in that a trans-esterification has been carried out between the lower alcohol and the phtalic acid ester and in that dioctyl phalate (DOP) is used as the said phtalic acid ester.

15

20

10. A procatalyst composition according to claim 9, characterized in that the transesterification has been carried out at a temperature in the range of 130°C to 140°C.

25

11. A procatalyst composition according to claim 9 or 10, characterized in that the transesterification has been carried out in a solvent having a boiling point above the transesterification temperature, preferably in nonane or decane.

30

12. A procatalyst composition according to claim 9, 10 or 11, characterized in that the lower alcohol is ethanol.

35

13. A procatalyst composition according to any of claims 9 to 12, characterized in that the titanium compound is  $TiCl_4$ .

14. A procatalyst composition according to any of claims 9-13, characterized in that it has been produced by  
a) reacting an adduct of  $\text{MgCl}_2$  and a lower alcohol with the titanium compound,

5 b) by reacting the product of step a) with dioctyl phthalate (DOP) under conditions in which a transesterification takes place between the dioctyl phthalate and the lower alcohol,

c) by washing the product or

10 d) by optionally reacting the product of step c) with a titanium compound.

15 15. A procatalyst composition according to any of claims 9-14, characterized in that 90% by weight of its particles have an average diameter with a length above 200  $\mu\text{m}$ .

20 16. A procatalyst composition according to any of claims 9-14, characterized in that its particles are agglomerates.

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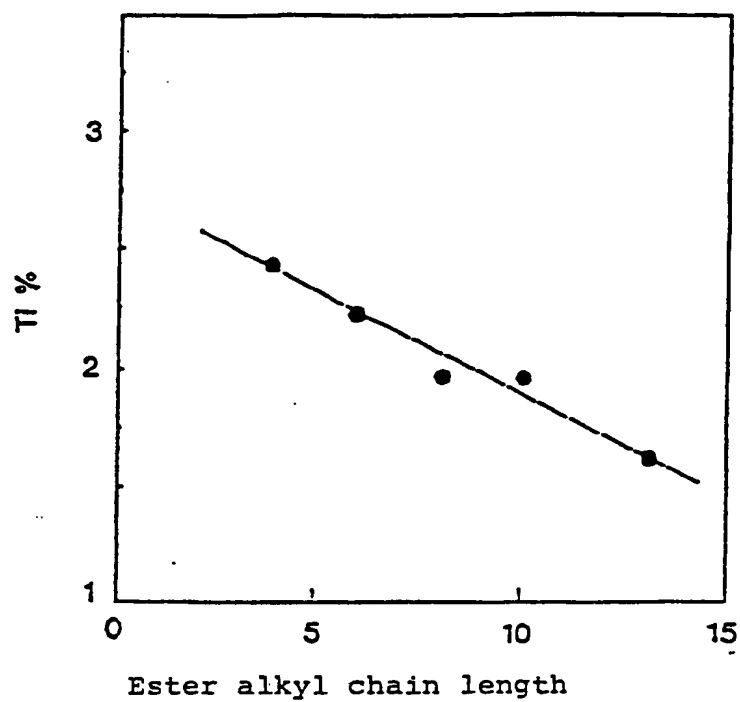


Fig. 1. Ti concentration in the catalysts as a function of the alkyl group chain length in the donor

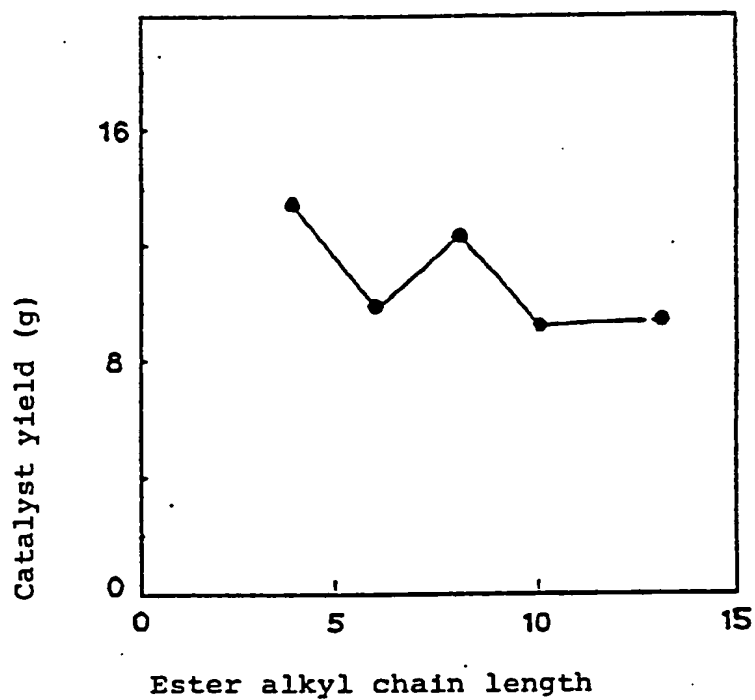


Fig. 2. Total catalyst yield of the catalyst synthesis as a function of the alkyl group chain length in the donor



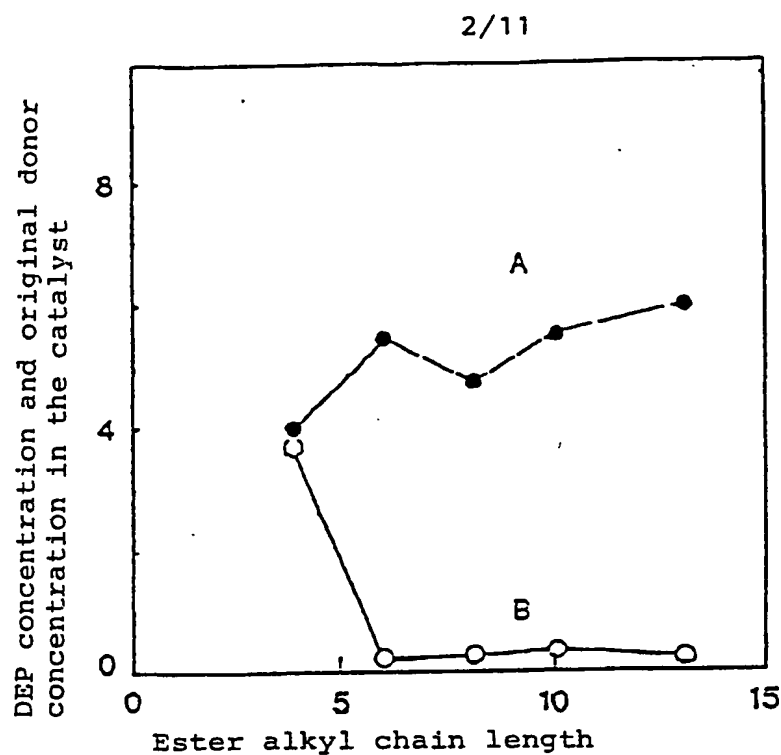


Fig. 3. Concentrations, produced in the catalyst synthesis, of the transesterified donor DEP (A) and the original donors (B)

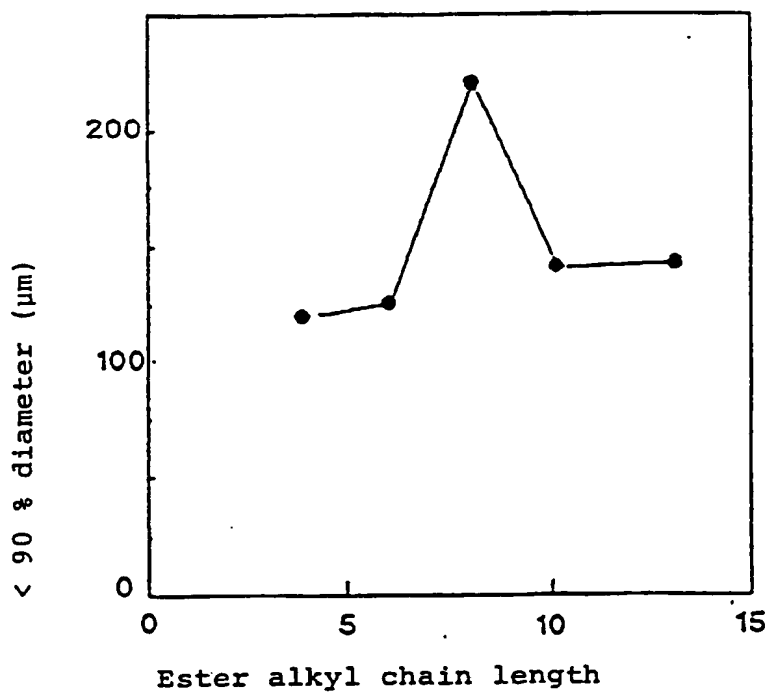


Fig. 4. Diameter of the large particle fraction (< 90 %) as a function of the alkyl group chain length in the donor.

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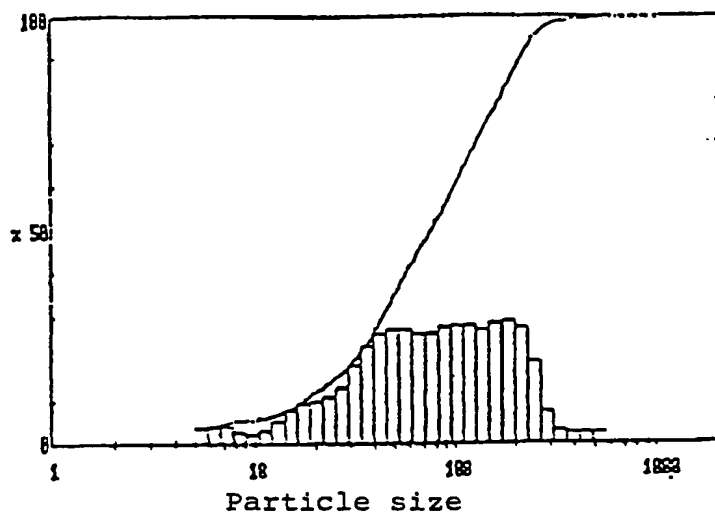


Fig. 5. Catalyst particle size distribution when octyl phthalate (C = 8) was used as an internal donor

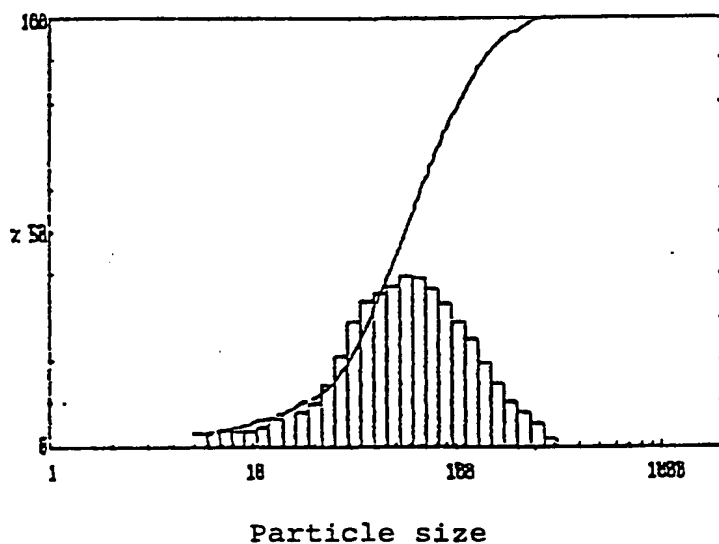


Fig. 6. Catalyst particle size distribution when decyl phthalate (C = 10) was used as an internal donor

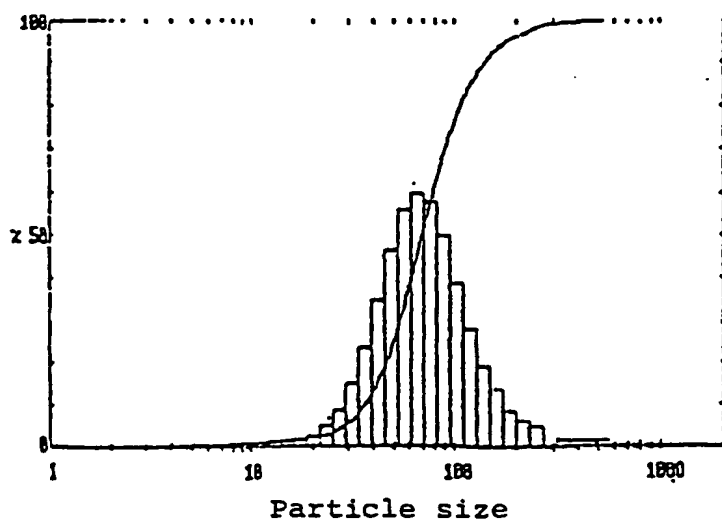


Fig. 7. Catalyst particle size distribution when tri-decyl phthalate (C = 13) was used as an internal donor

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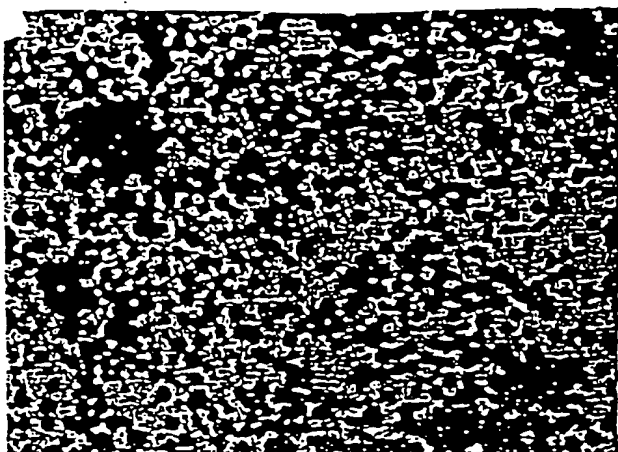


Fig. 8. Microscope picture of the catalyst C-C-4.  $C = 4$ , unit =  $25\mu\text{m}$

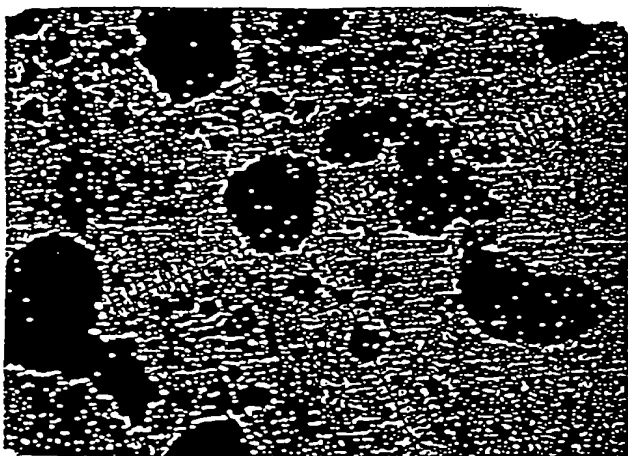


Fig. 9. Microscope picture of the catalyst C-C-8.  $C = 8$ , unit =  $50\mu\text{m}$

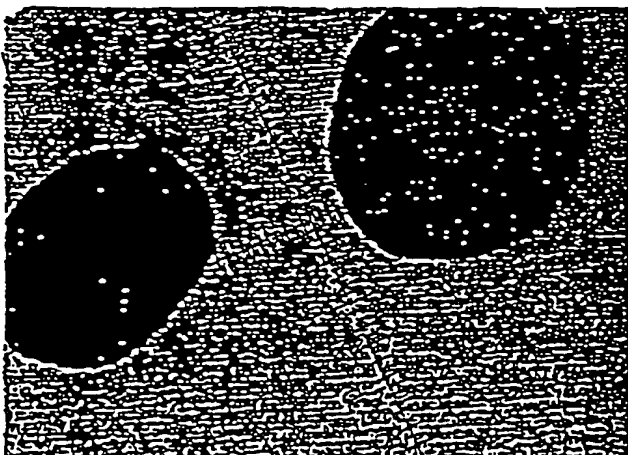


Fig. 10. Microscope picture of the catalyst C-C-10.  $C = 8$ , unit =  $50\mu\text{m}$

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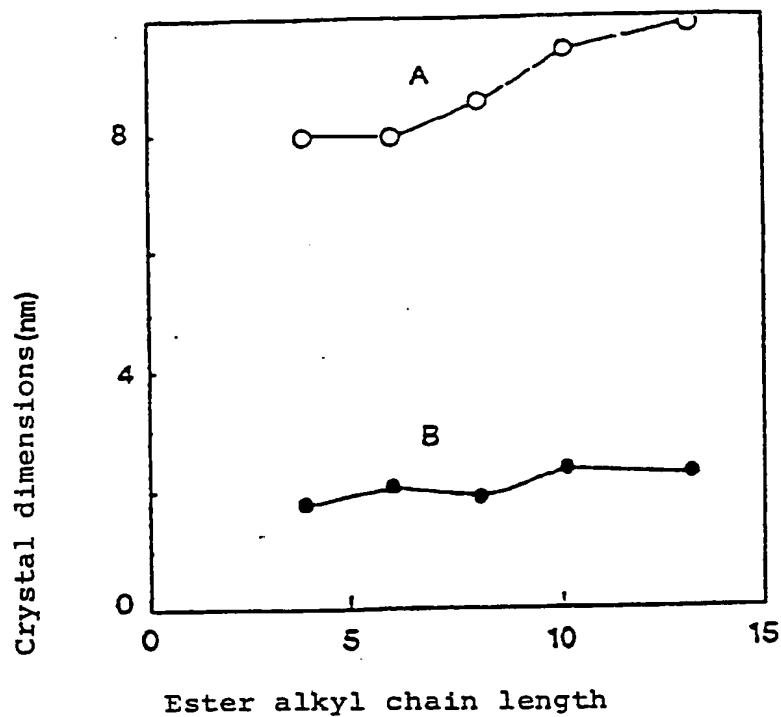


Fig. 11. Width (A) and height (B) of the  $MgCl_2$  crystal as a function of the alkyl group chain length in the donor

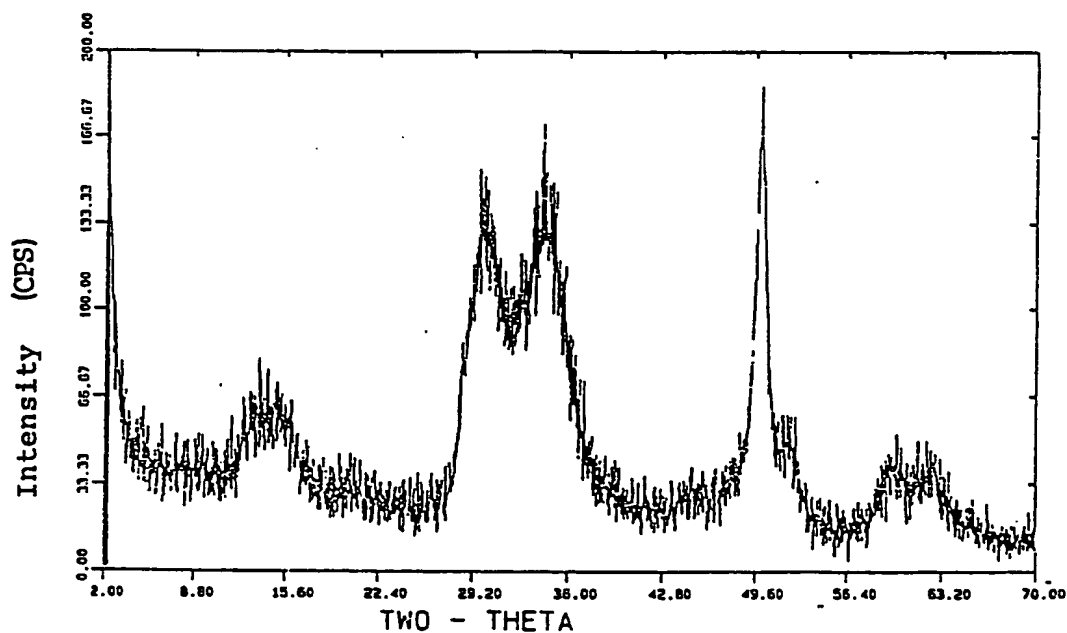


Fig. 12. X-ray pattern of the catalyst C-C-6, in which internal donor prHP has been transesterified to DEP. A double peak is observable at 13-15°.

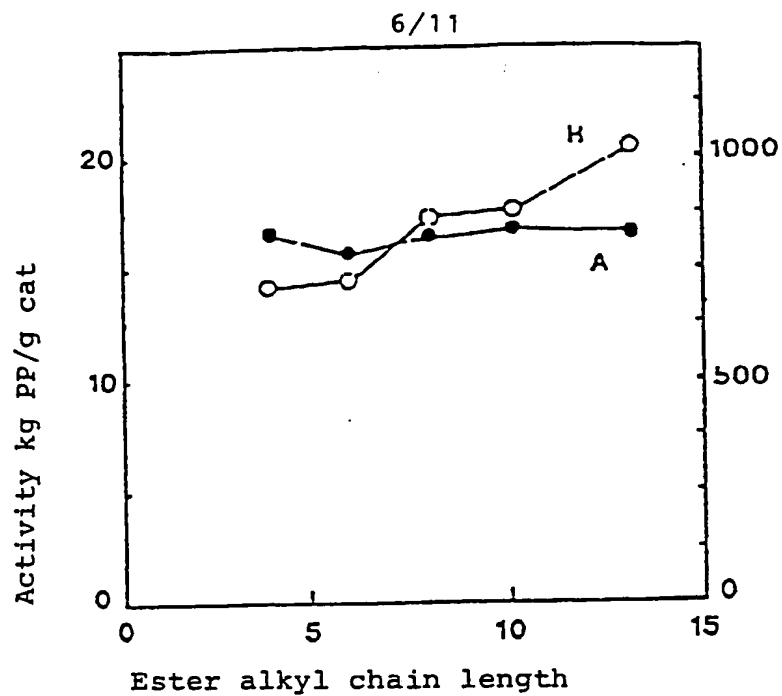


Fig. 13. Catalyst activity as a function of the alkyl group chain length in the donor. Curve (A) refers to the unit kg PP/g cat. and curve (B) to the unit kg PP/g Ti

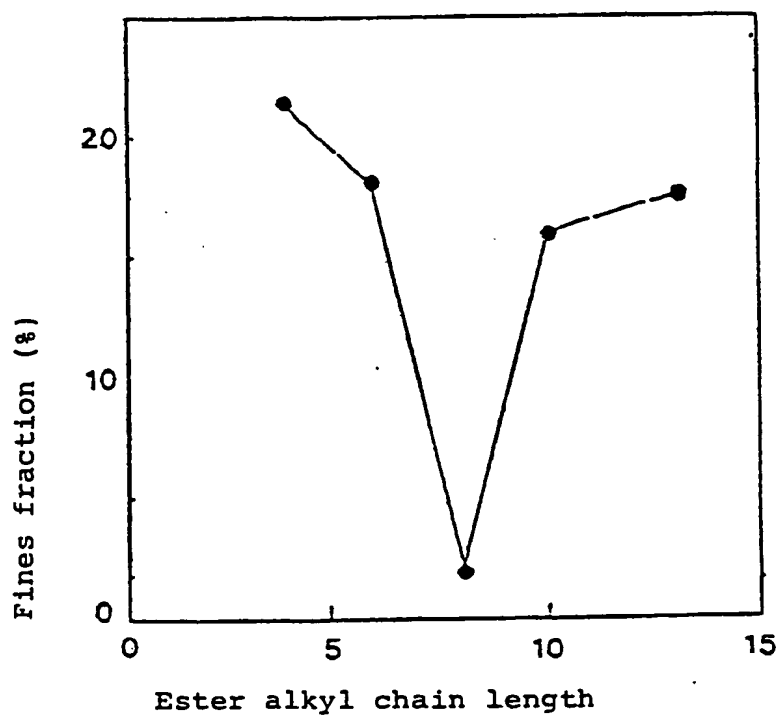


Fig. 17. Total amount of fines fraction ( $d < 1\text{mm}$ ) as a function of the alkyl group chain length in the donor

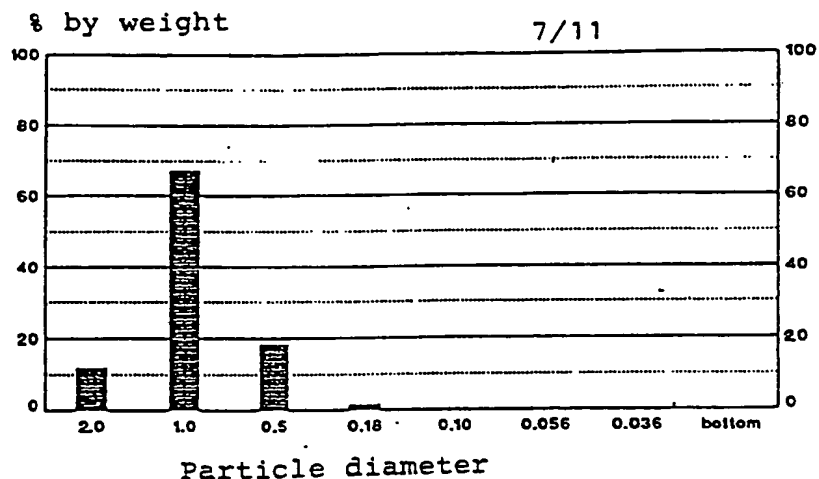


Fig. 14. Particle size distribution of the polymer PP-C-4  
(C = 4)

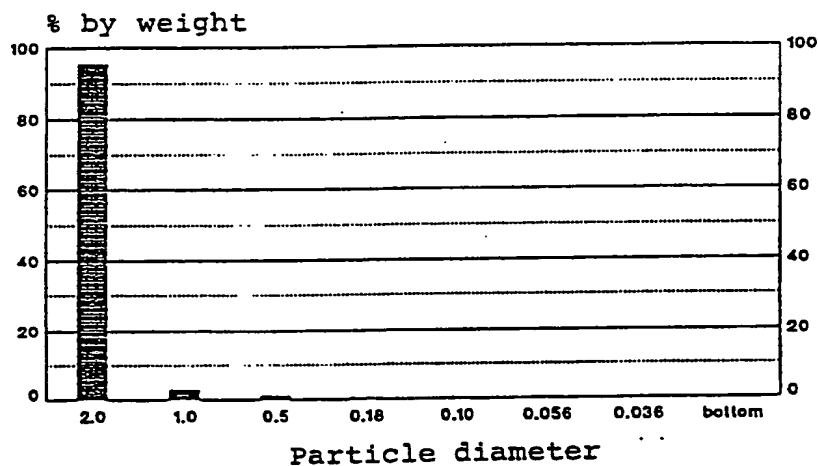


Fig. 15. Particle size distribution of the polymer PP-C-8  
(C = 8)

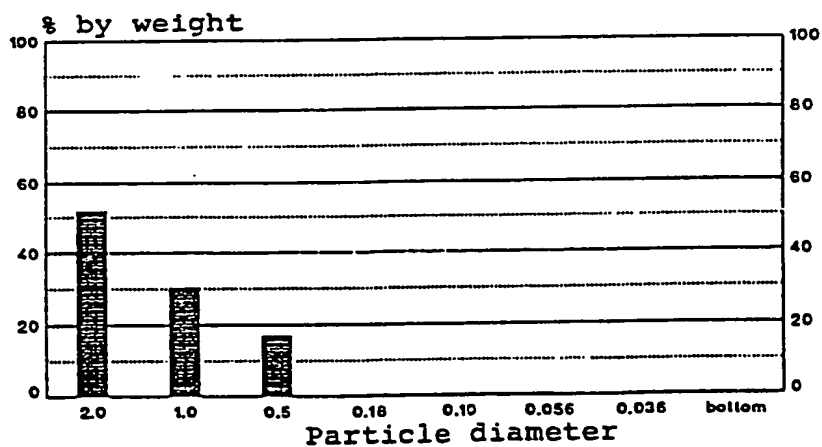


Fig. 16. Particle size distribution of the polymer PP-C-13  
(C = 13)

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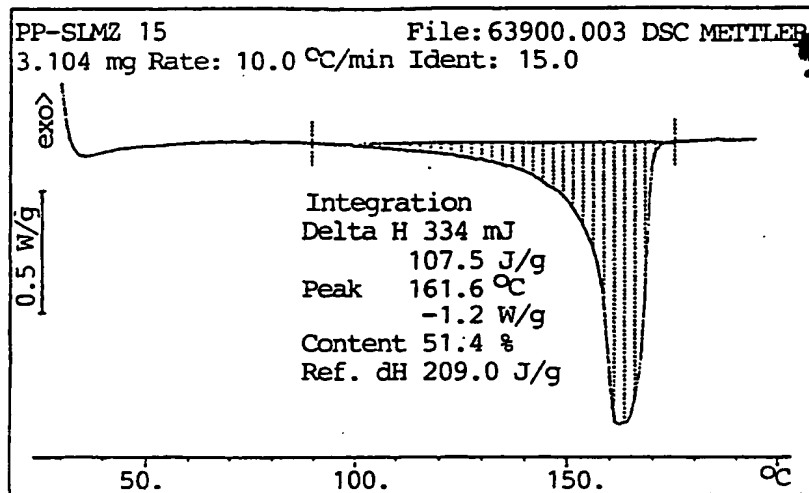


Fig. 19.  
DSC (differential scanning calorimeter) curve of the polymer PP-C-4

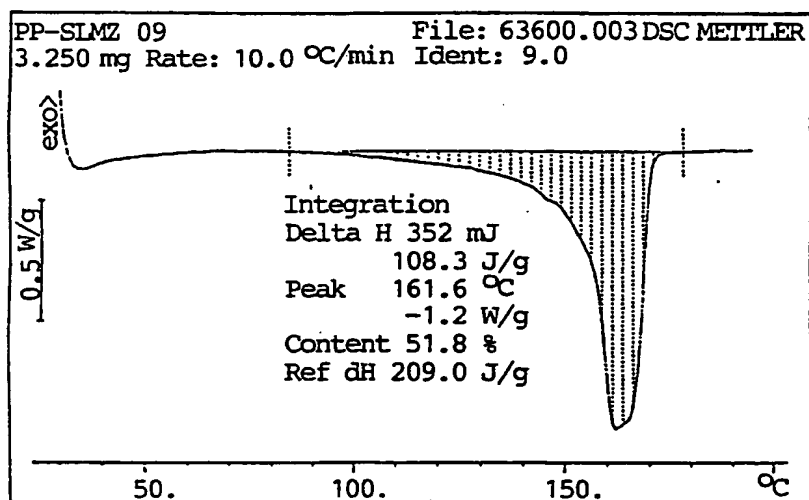


Fig. 20.  
DSC curve of the polymer PP-C-8

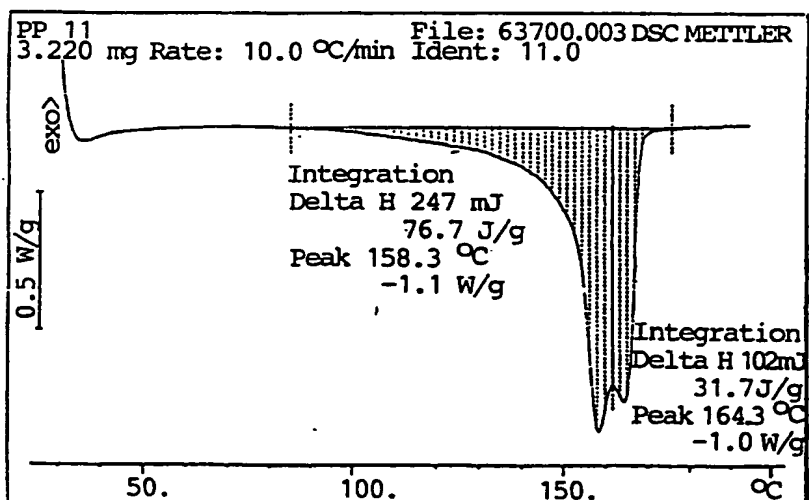


Fig. 21.  
DSC curve of the polymer PP-C-13

SUBSTITUTE SHEET

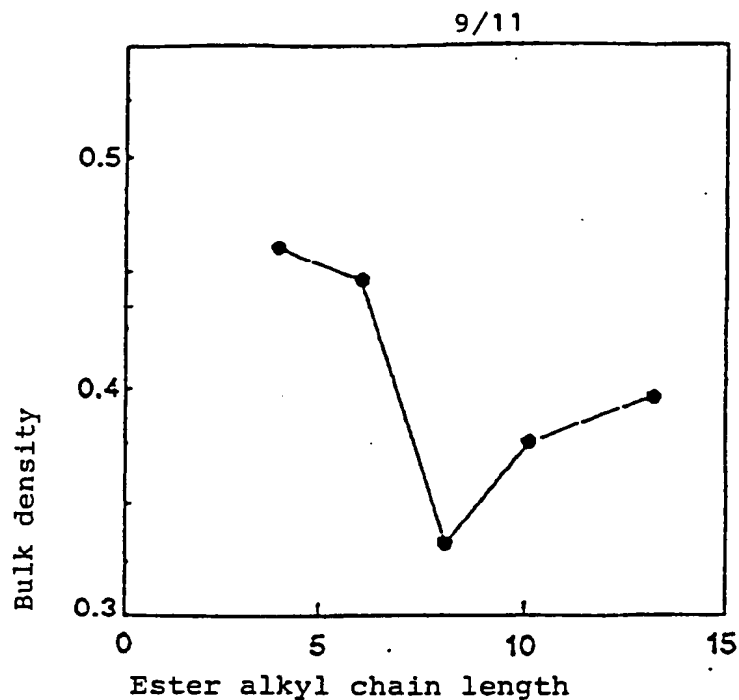


Fig. 18. Bulk density of the polymers as a function of the alkyl group chain length in the donor

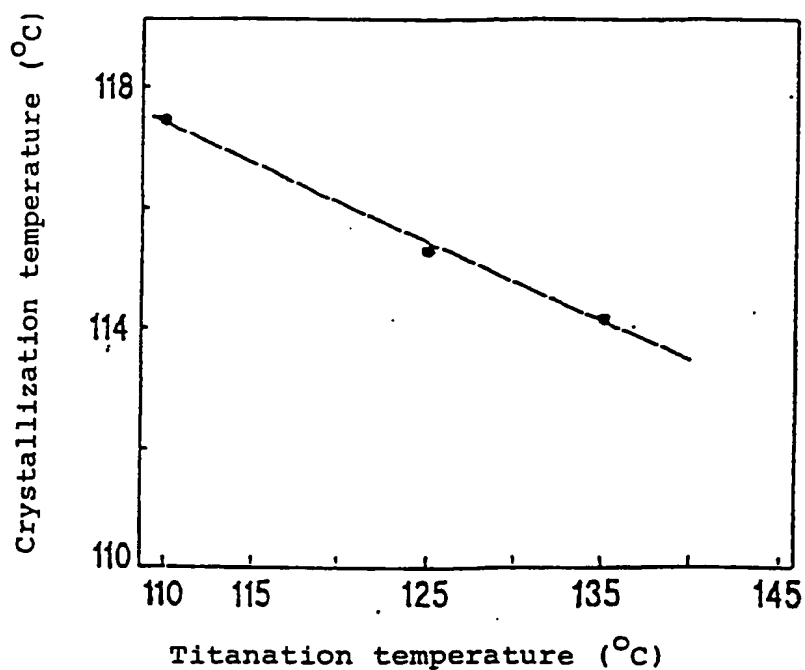


Fig. 22. Crystallization temperature of polypropylene as a function of the titanation ( $\text{TiCl}_4$  treatment) temperature used in the catalyst synthesis



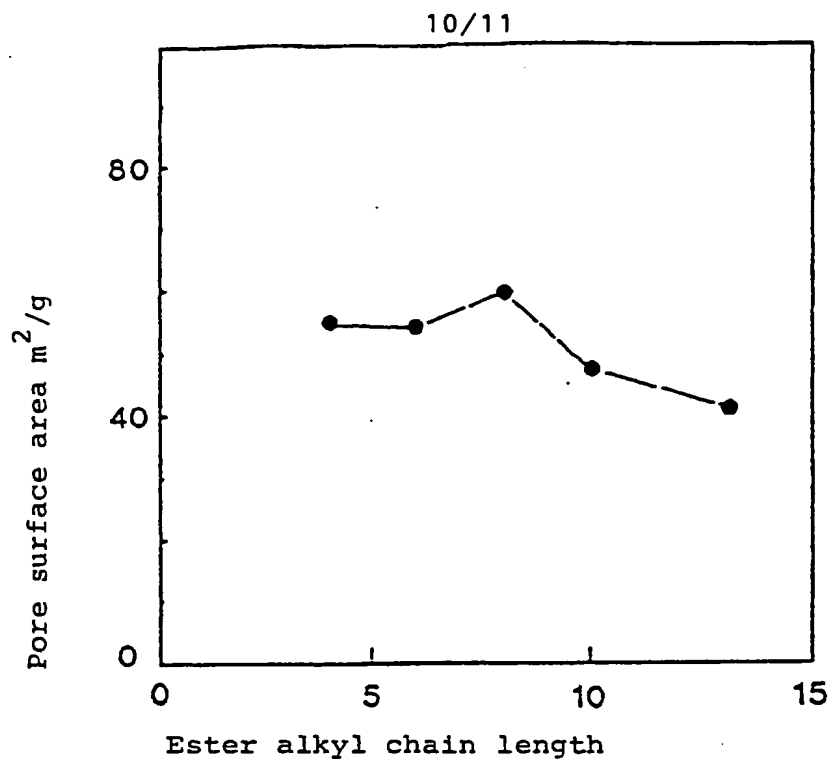


Fig. 23. Pore surface area ( $\text{m}^2/\text{g}$ ) in the polymers as a function of the alkyl group chain length in the donor

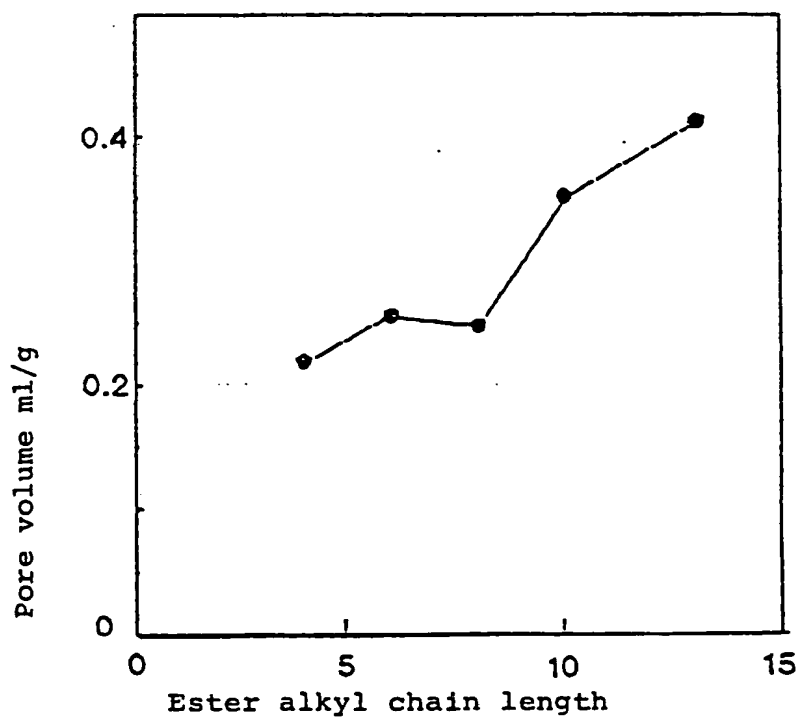


Fig. 24. Pore volume ( $\text{ml/g}$ ) in the polymers as a function of the chain length of the alkyl group in the donor

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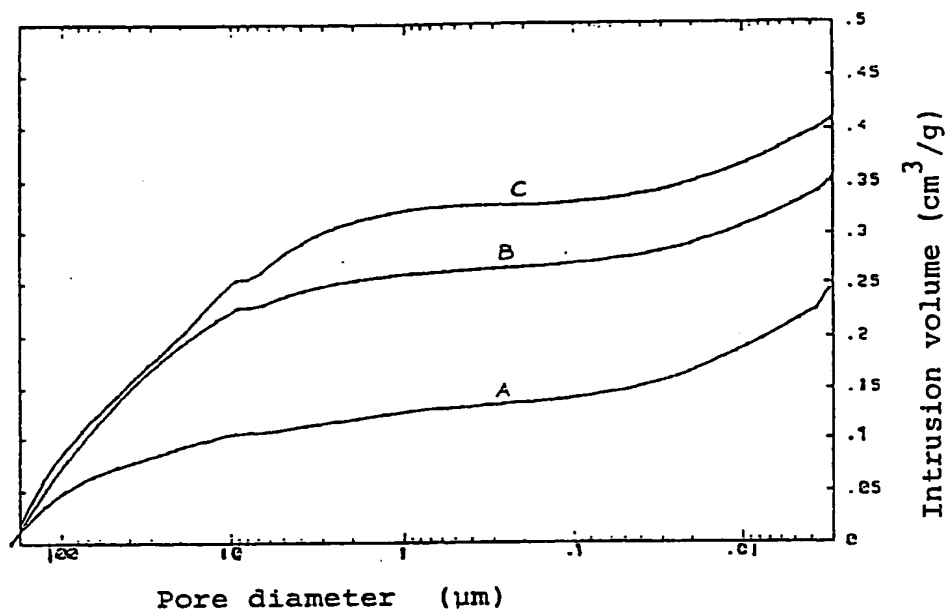


Fig. 25. Pore volume distributions of polymers PP-C-8 (A), PP-C-10 (B) and PP-C-13 (C)

# INTERNATIONAL SEARCH REPORT

International Application No PCT/FI 92/00082

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC5: C 08 F 10/00, C 08 F 4/651, 4/654		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC5	C 08 F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched <sup>8</sup>		
SE,DK,FI,NO classes as above		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
E	EP, A3, 0488537 (NESTE OY) 3 June 1992, see page 1, line 35 - line 40; claims 1,2-9,12 example 1 --	1-7,9-10,12-14
X	EP, A1, 0226003 (BASF AKTIENGESELLSCHAFT) 24 June 1987, see column 4, line 4 - line 35; claim 1 example 1 --	1-5,7,9-10,12-14
A	WO, A1, 8707620 (NESTE OY ET AL.) 17 December 1987, see claims 1-3 --	1-4,7,9,12-14
A	DK, B, 160256 (MONTEDISON S.P.A.) 18 February 1991, example 19 -- -----	1-4,7,9,12-14
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
14th August 1992	1992 -08- 21	
International Searching Authority	Signature of Authorized Officer	
SWEDISH PATENT OFFICE	Agneta Österman Wallin	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. PCT/FI 92/00082**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 01/07/92. The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A3- 0488537	92-06-03	NONE	
EP-A1- 0226003	87-06-24	DE-A- 3540699	87-05-27
		JP-A- 62119208	87-05-30
		US-A- 4761461	88-08-02
WO-A1- 8707620	87-12-17	CH-A-B- 671767	89-09-29
		DE-T- 3790287	88-06-23
		EP-A- 0279818	88-08-31
		GB-A-B- 2199767	88-07-20
		JP-T- 63503550	88-12-22
		NL-T- 8720292	88-04-05
		SE-B-C- 458927	89-05-22
		SE-A- 8800363	88-02-05
		US-A- 4829034	89-05-09
DK-B- 160256	91-02-18	NONE	